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**Homogeneous
freezing of organic
aerosol particles**

B. Kärcher and T. Koop

The role of organic aerosols in homogeneous ice formation

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Abstract

Recent field observations suggest that the fraction of organics containing aerosol particles in ice cloud particles is diminished when compared to the background aerosol prior to freezing. In this work, we use model calculations to investigate possible causes for the observed behavior. In particular, homogeneous freezing processes in cooling air parcels containing aqueous inorganic particles (represented by sulfuric acid) and organic particles (represented by pure malonic acid and mixed malonic/sulfuric acid) are studied with a detailed microphysical model. A disparate water uptake and resulting size differences that occur between organic and inorganic particles prior to freezing are identified as the most likely reason for the poor partitioning of organic aerosols into the ice phase. The differences in water uptake can be caused by changes in the relationship between solute mass fraction and water activity of the supercooled liquid phase, by modifications of the accommodation coefficient for water molecules, or by a combination thereof. The behavior of peak ice saturation ratios and total ice crystal number concentrations is examined, and the dependence of the results on cooling rate is investigated. Finally, processes are discussed that could possibly modify the homogeneous freezing behavior of organic particles.

1. Introduction

Atmospheric aerosols often consist of varying mixtures of organic and inorganic compounds (Duce et al., 1983; Saxena and Hildemann, 1996; Murphy et al., 1998). The organic species are found at times to account for up to 50% of the total dry aerosol mass in the boundary layer as well as the free troposphere (Novakov et al., 1997; Middlebrook et al., 1998; Murphy et al., 1998; Lee et al., 2002). Furthermore, in upper tropospheric aerosols the organics are usually internally mixed with sulfate, with organic constituents contributing 10–50% of the solute mole fraction (Murphy et al., 1998; Lee et al., 2002). The chemical nature of these organics is quite diverse, but

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several field and modeling studies have suggested that dicarboxylic acids are a significant component of the organic fraction (Gill et al., 1983; Saxena and Hildemann, 1996; Chebbi and Carlier, 1996; Yao et al., 2002).

The possible impact of organic constituents on the interplay of atmospheric aerosol particles with water vapor and clouds have been investigated. For example, organics affect the hygroscopicity of aerosols (Cruz and Pandis, 2000; Dick et al., 2000; Ming and Russell, 2002) as well as the formation and properties of cloud droplets (Novakov and Penner, 1993; Facchini et al., 1999).

In contrast, the effects of organics on the ice nucleation behavior of upper tropospheric aerosols is less well studied. Laboratory studies have indicated that homogeneous freezing of low molecular weight dicarboxylic acids is not as efficient as for sulfate aerosol (Prenni et al., 2001). Simultaneous measurements of ice cloud particles and chemical identification of aerosols have been made in the field (Cziczo et al., 2004a,b; DeMott et al., 2003). These measurements revealed that organic-containing aerosols are less abundant than sulfate aerosols in ice cloud particles when compared to the interstitial aerosols, suggesting that organics might hamper ice nucleation. At present, the reason for this behavior is not clear. This uncertainty stems in part from the lack of molecular information on the organics that are contained in the observed aerosols.

Here, we present the first attempt to provide a basic theoretical understanding of the processes at work during the homogeneous formation of the ice phase in mixtures of inorganic and organic aerosols. To this end, we use a microphysical parcel model to study the effects of organics on homogeneous ice nucleation in liquid aerosols at upper tropospheric conditions as well as the resulting ice particle properties. We use a dicarboxylic acid, malonic acid ($\text{HOOC-CH}_2\text{-COOH}$), as a surrogate for the organics. In addition, we vary important aerosol properties such as the mean particle size and water accommodation (or condensation) coefficient in order to make our results applicable also to other organics of atmospheric relevance.

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2. Model description

2.1. Microphysical model

We use the detailed microphysical model APSC*m* (Kärcher, 2003) to simulate aerosol particle growth and evaporation, homogeneous ice nucleation, ice particle growth and sublimation. The model is used in a parcel mode with prescribed constant cooling rates dT/dt .

Aerosol and ice particle size distributions are discretized over 100 size bins with a constant bin-volume ratio of 1.35, starting at a minimum particle radius of 5 nm. Aerosol growth is treated in a Lagrangian manner while ice particle growth is treated using a moving-center size structure. Inorganic and organic particles are prescribed as distinct types and are distributed lognormally, each with a total number of 100 cm^{-3} , a mode radius R of $0.1\text{ }\mu\text{m}$, and a geometric width of 1.5. Variable time steps $\Delta t[\text{s}] = (dT/dt)^{-1} [\text{K h}^{-1}]$ are sufficiently small to yield accurate numerical solutions.

For organic particles, the condensation coefficient α is varied, and for inorganic particles (assumed to consist of aqueous sulfuric acid, $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$) we chose $\alpha=1$, which is consistent with recent laboratory measurements (Gershenson et al., 2004). While for some applications we study the behavior of each particle type in isolation, we focus on the fraction η of organic particles that contribute to the total number density n_i of ice crystals formed.

To describe homogeneous ice nucleation and freezing of aqueous aerosols in the APSC*m*, we use the water-activity-based model by Koop et al. (2000). This model is based on an evaluation of ice nucleation measurements of 18 types of solutes including several organics. It has the advantage that it only requires knowledge of the water activity of a particular aerosol solution particle at any given temperature in order to calculate the corresponding ice nucleation rate coefficient. In the APSC*m*, the water activity is calculated for each aerosol type as a function of particle size.

In our model, ice nucleation is described as a volume dependent nucleation process. Recently, pseudo-heterogeneous surface nucleation of ice has been proposed as an

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alternative mechanism (Djikaev et al., 2002; Tabazadeh et al., 2002). We note that organics might also influence this ice nucleation process through changes in particle surface tension (compare Djikaev et al., 2004). However, because of the remaining uncertainties associated with the surface nucleation mechanism, we restrict our model calculations to homogeneous volume dependent nucleation of ice. With this nucleation model, the APSC_m has been shown to be suitable for the description of homogeneous freezing of sulfuric acid aerosol particles (Haag et al., 2003). In our present analysis, we make use of this model for all organic aerosols as well. Therefore, we can investigate what aerosol properties can lead to preferential ice nucleation of sulfuric acid over organic aerosols, even if the nucleation model is identical for both particle types.

In most simulations we use $dT/dt=10\text{ K h}^{-1}$, a value where non-equilibrium effects influence liquid aerosol water content and homogeneous freezing. Atmospheric observations suggest that such rapid cooling rates are caused by mesoscale variability in vertical wind speeds and occur rather frequently at mid- and low latitudes in cirrus conditions (Kärcher and Ström, 2003; Jensen and Pfister, 2004; Haag and Kärcher, 2004; Luo et al., 2004). However, we will also address the impact of smaller and higher cooling rates on our results.

The temperatures T reported in this work are approximate freezing temperatures in the model, extending from warm (230 K) to cold (200 K) conditions. For simplicity, we let ice formation take place near 200 mb in all cases, because our results are insensitive to variations of upper tropospheric pressure.

2.2. Aerosol thermodynamic models

We have chosen sulfuric acid and malonic acid as the representatives for inorganic and organic constituents of upper tropospheric aerosols. While the occurrence of H_2SO_4 is well established through field data (e.g., Murphy et al., 1998, and references therein), the chemical nature of organics found in upper tropospheric aerosols is less clear and still an open issue. As mentioned in Sect. 1, the organics will most likely consist of a distribution of several organic species. On the other hand, organic acids seem to

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constitute a major fraction of the organics (Gill et al., 1983; Saxena and Hildemann, 1996; Chebbi and Carlier, 1996; Yao et al., 2002).

Because of the lack of quantitative in situ data, we have chosen malonic acid for two reasons: first, the thermodynamic properties of aqueous solutions of malonic acid at low temperature are better established than for most other organics of interest, and secondly, malonic acid is the smallest dicarboxylic acid with a large solubility in water, and it is miscible with inorganic solutes over a wide range of concentrations (Brooks et al., 2002; Ming and Russell, 2002; Wise et al., 2003; Marcolli et al., 2004).

In our simulations, we investigate three cases of aqueous solutions, pure aqueous sulfuric acid (SUL), pure aqueous malonic acid (MAL), and a 1:1 mole ratio mixture of sulfuric acid/malonic acid (SUL/MAL). We frequently refer to the first type as “inorganic” and to the two latter types as “organic”.

To perform simulations with such aerosols in the APSC m , the water vapor pressure of aqueous solutions of these solutes are required over a wide concentration range to low temperatures (~ 200 K). The vapor pressure of H₂SO₄/H₂O solutions has been calculated using the parameterization by (Luo et al., 1995). Since neither data nor parameterizations exist for aqueous malonic acid solutions at low temperatures, we have used experimental data to develop such a parameterization. We have used the data by (Peng et al., 2001) at room temperature to establish a solute mass fraction versus water activity relationship, and the data by (Braban et al., 2003) to parameterize its temperature dependence for the extrapolation to low temperatures. The latter data are in agreement with very recent measurements by Parsons et al. (2004). We have used both pure binary parameterizations to calculate the water vapor pressure of mixed ternary aqueous solutions of sulfuric acid/malonic acid with a 1:1 solute mole ratio. This has been done using the approach by Zdanovskii, Stokes, and Robinson (Seinfeld and Pandis, 1998), which has been shown to work successfully in ammonium sulfate/malonic acid mixtures at room temperature (Choi and Chan, 2002; Prenni et al., 2003). Finally, we have used the above solution vapor pressures in the limit of vanishing solute mass fractions to compute the vapor pressure of pure water and hence water

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activity for reasons of internal consistency.

In Fig. 1 we show the a_w versus solute mass fraction W relationships resulting from our calculations for pure aqueous sulfuric acid (SUL), the 1:1 sulfuric acid/malonic acid mixture (SUL/MAL), and pure aqueous malonic acid (MAL) at three different temperatures T (colored coded). The mixed particle type SUL/MAL interpolates between the pure components SUL (hygroscopic) and MAL (less hygroscopic); note that W -axis scales change. The filled circles (same color coding) indicate at which combination of a_w and W homogeneous freezing commences under equilibrium conditions based on the water activity model.

The accommodation coefficient α for the different solutions is unclear. While $\alpha=1$ is reasonable for aqueous sulfuric acid at low temperatures (Gershenson et al., 2004; Clement et al., 1996), the presence of organic solutes might reduce α significantly (Gill et al., 1983; Xiong et al., 1998)

Before we present and discuss the results in Sect. 3, we note that we have performed similar calculations with polyols instead of malonic acid. The investigated polyols were oligomers of poly[ethylene glycol] with a molar mass of 300 g mol^{-1} , PEG300. Although the quantitative results for the PEG300 system are slightly different, the key processes and pathways of freezing modification are very similar to the malonic acid system. This increases confidence in applying our findings to real atmospheric situations with variable types of organics, as described in Sect. 4.

3. Results and discussion

3.1. Aerosol composition affects particle size

Let us first assume thermodynamic equilibrium between the ambient relative humidity (RH) and the liquid aerosol particles at all times, i.e., $a_w = RH/100\%$. Then Fig. 1 tells us that the particles are less water-rich when the amount of organic solute is larger. Furthermore, the aerosol water content decreases with decreasing T . A direct implica-

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tion of this behavior is that the organic-containing particles remain smaller in a cooling air parcel than the more hygroscopic sulfuric acid particles. This is consistent with a thermodynamic modeling study which shows that the presence of malonic acid reduces the growth of ammonium sulfate particles (Ming and Russell, 2002). In addition, very small particles will have lower a_w than larger ones owing to the Kelvin barrier (Seinfeld and Pandis, 1998; Haag et al., 2003).

On the other hand, also kinetic effects have an impact on the water content and a_w of aerosol particles. For example, at low cooling rates, all particles will actually stay close to water equilibrium. However, very large particles will have lower a_w than smaller ones due to diffusion limitations of the water condensation rate. The latter non-equilibrium effect becomes more important when the cooling rate is high and T is low. Both, thermodynamic and kinetic effects have been modeled for aqueous sulfuric acid particles (Haag et al., 2003), in close agreement with measurements (Möhler et al., 2003).

In sum, we emphasize that both, different thermodynamic properties of aerosol particles and kinetic effects are expected to result in a size separation between more and less hygroscopic particles that coexist in cooling air parcels. We demonstrate below that this size separation crucially impacts the contribution of each particle type to ice formation.

3.2. Aerosol composition affects freezing fractions

Next, we describe the results from the parcel simulations. In most of these simulations the aerosol is composed of two externally mixed modes with identical dry size distributions (distinct number concentrations). Each mode is allowed to have different hygroscopic properties and water condensation coefficients. It is very instructive to study first two separate modes that both consist of $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ aerosols, with identical hygroscopic properties. However, we vary α from 0.0001 to 1 for one of the two modes for didactical purposes. Recall that η is the fraction of frozen aerosol particles with variable α relative to the total number of frozen particles.

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Figure 2a depicts the results for η as a function of α for the two SUL modes (hereafter referred to as case SUL+SUL). As both aerosol modes have identical sizes (solid curves), $\eta=0.5$ when α approaches unity, because then both modes freeze in the same proportion. All solid curves in Fig. 2a would remain at $\eta=0.5$ for all values of α if the $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ particles were in full thermodynamic equilibrium at all times, in which case $a_w = RH/100\%$, regardless of size (apart from the Kelvin effect, which is unimportant in most of our simulations, confer Sect. 3.4).

However, fewer droplets freeze from the mode with reduced α because of reduced uptake of H_2O molecules during the cooling phase. This is due to the fact that these particles are less dilute and have smaller volumes than those with $\alpha=1$. This markedly reduces their probability to freeze homogeneously for $\alpha \lesssim 0.05$ –1, depending on T . At low T , equilibrium is approached later, as the H_2O vapor pressure decreases exponentially. (The characteristic timescale of equilibration of H_2O by gas phase transport of H_2O molecules to the aerosol particles is inversely proportional to the H_2O vapor pressure.) For our choice of dT/dt , this effect becomes important only at $T < 215\text{ K}$, as the red (215 K) and black (230 K) curves are almost identical. In Sect. 3.5 we will examine the role of dT/dt in more detail.

We conclude from this exercise that non-equilibrium (kinetic) and size effects are intimately coupled. A size separation between particles with different water uptake properties must arise in a cooling air parcel. This size separation ultimately influences the freezing process even if the particle size distributions are identical prior to cooling.

The impact of initial differences in particle size is analyzed by discussing the dashed and dash-dotted curves in Fig. 2a, where we have increased and decreased R from the particles with variable α by a factor of 2, respectively, at $T=215\text{ K}$. More (fewer) of these droplets freeze when they are initially larger (smaller). The effect of initial differences in particle size is quite dramatic, and decides which of the two particle modes wins the freezing competition, regardless of α . It is more pronounced at low T , where the kinetic effects are magnified. As shown at the end of this section, this effect occurs between chemically different aerosols as well.

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Next, we investigate how differences in the hygroscopic properties of the two particle modes effect the water uptake, size, and freezing properties of the aerosol populations. In Figs. 2b and c, the second mode of particles with variable α are composed of the 1:1 mixture of sulfuric and malonic acid (SUL/MAL) or pure malonic acid (MAL), respectively, so that η denotes the fraction of ice particles that nucleated on organic-containing particles. The first mode remains to consist of aqueous sulfuric acid particles with $\alpha=1$.

The principal behavior $\eta(\alpha)$ for the organic cases is similar to case SUL+SUL, but we observe differences in detail which are caused by differences in a_w between inorganic and organic species (recall Fig. 1). Typically, the organic aerosols do not freeze preferentially, as $\eta < 0.5$ regardless of α or T (solid curves). The computed η -values are not sensitive to α unless $\alpha \lesssim 0.05$ – 0.1 , depending on T .

In contrast to case SUL+SUL, the solid curves differ in the limit $\alpha \rightarrow 1$, especially in case SUL+MAL, caused by the differences in hygroscopic properties of the particles. The case SUL+SUL/MAL can be considered as an intermediate case, in which the freezing properties are still largely dominated by H_2SO_4 in the mixed particles. The simulations start at water equilibrium, where the organic mass fraction W adjusts such that $a_w(W, T) = RH/100\%$ for all droplets. As W is proportional to particle volume (apart from density effects), mean sizes of inorganic and organic droplets will be different inasmuch as their $a_w(W, T)$ are different. The organic particles are smaller than the H_2SO_4 particles (Fig. 1). This size effect becomes more pronounced as T decreases and yields different η in the limit $\alpha \rightarrow 1$.

The effect of initial size differences between SUL, SUL/MAL, and MAL particles are similar to Fig. 2a. We point out that the organic particles might freeze preferentially over H_2SO_4 when they are sufficiently large (dash-dotted curves in Figs. 2b and c).

3.3. Aerosol composition affects freezing relative humidity and ice crystal concentrations

Figure 3a shows the peak saturation ratios over ice, S_i , for four cases (SUL, SUL/MAL, MAL, SUL+SUL/MAL) as a function of α and different freezing temperatures. Note that

only the case SUL+SUL/MAL consists of two separate particle modes.

Peak values of S_i are generally higher than the freezing onset values (not shown), the difference increasing with decreasing T , consistent with laboratory measurements and previous modeling studies (Möhler et al., 2003; Haag et al., 2003).

5 The SUL case with $\alpha=1$ is displayed with single filled circles. When organic solute is present (cases SUL/MAL and MAL), the peak (and onset) S_i increases when α becomes smaller than ~ 0.05 – 0.1 . For small α , water uptake and, thus, freezing is retarded, allowing higher supersaturations to be reached. In such cases, the differences between onset and peak RHI can reach 8% (case MAL for $\alpha=0.001$ at 200 K). An exception is the system SUL+SUL/MAL, where changes of α have no effect on S_i which rather stays constant and close to the value obtained for case SUL. This is because ice formation occurs predominantly in the pure H_2SO_4 particles, see Fig. 2b, rendering the presence of externally mixed SUL/MAL particles unimportant for the freezing process.

10 An important atmospheric implication of these calculations is that the supersaturations required for homogeneous freezing of organic-rich particles can be substantially higher (by more than 0.1) than those for pure $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$, but only in cases when no (or very few) separate $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ particles are available for freezing. For example, we find that less than $\sim 0.05 \text{ cm}^{-3}$ SUL particles must be present in a SUL+SUL/MAL particle population at a freezing temperature of 200 K in order to obtain a peak value $S_i=1.78$ that coincides with the peak value obtained for pure SUL/MAL particles. The peak ice saturation is close to the pure SUL limit of $S_i=1.61$ in the same particle population when the concentration of SUL particles increases above 10 cm^{-3} . We reiterate this issue in Sect. 4.

25 Figure 3b shows the total number density of ice crystals, n_i , that nucleate from the aerosol types discussed in Fig. 3a. In general, n_i increases with decreasing T as growth rates of pristine ice particles are smaller at low T , causing a slower depletion of gaseous H_2O and more available time for additional particles to freeze. Again, the filled circles denote the pure $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ case. For the organic particles SUL/MAL and MAL, n_i starts to increase substantially when $\alpha < 0.1$. At the coldest temperature, n_i

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decreases again for $\alpha < 0.006$ (SUL/MAL) or $\alpha < 0.0025$ (MAL). Here, the water condensation rate onto aerosol particles becomes so small that only a limited number of particles can freeze, namely those large enough to take up water molecules despite the Kelvin barrier and small enough to take up water molecules despite diffusion limitations.

In contrast, the system SUL+SUL/MAL does not lead to significant changes of n_i , and the crystal concentration stays close to case SUL, except for a slight enhancement at $\alpha \sim 0.1$.

3.4. Aerosol composition affects freezing aerosol size distributions

Interpretation of the results shown in Fig. 3 is supported by inspecting the freezing aerosol size distributions for selected cases, see Fig. 4. The freezing aerosol size distribution is defined as the difference between the aerosol number size distributions before and after freezing, displayed versus the dry particle diameter D .

The initial distributions are shown as black curves for the case SUL+SUL/MAL (left column), and for the cases SUL/MAL (middle column) and MAL (right column). The frozen particle distributions are plotted as solid curves (case SUL+SUL/MAL has two additive modes – solid curves: SUL, dashed curves: SUL/MAL). Also shown as filled circles are the freezing size distributions for case SUL (assuming $\alpha = 1$) to guide the eye. As before, red curves are for 230 K and blue curves for 200 K.

For the simulations with $\alpha = 0.1$ (top panel in Fig. 4), freezing aerosol spectra are similar to the pure $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ case over a wide range of T . Only slight differences between SUL and SUL/MAL (middle column) and between SUL and MAL (right column) are notable. This is consistent with Fig. 3 when $\alpha > 0.05$ (230 K) $\alpha > 0.1$ (200 K), i.e., in regions where S_i and n_i do not change significantly.

We now consider the case $\alpha = 0.001$ (bottom panel in Fig. 4), i.e., organic particles with a rather small water accommodation coefficient. If SUL and SUL/MAL are present as distinct particle types, then the organic particles do not contribute to freezing if α is small, and do not alter cirrus properties (left column).

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However, the properties of cirrus clouds nucleating on organic particles SUL/MAL or MAL in the absence of SUL may strongly differ from pure SUL in terms of S_i and n_i for sufficiently small α . Figure 4 demonstrates that the freezing aerosol distribution is shifted towards small particle sizes, where freezing at 200 K becomes eventually limited by the Kelvin effect, see left tails of the blue distributions in the cases SUL/MAL and MAL for $\alpha=0.001$. These results for low α and low T are somewhat uncertain because, in the absence of precise data, we have used the surface tension for $\text{H}_2\text{SO}_4/\text{H}_2\text{O}$ to calculate the Kelvin barrier for SUL/MAL and MAL.

In cases SUL/MAL and MAL, the large particles that freeze when $\alpha=0.1$ stay liquid when $\alpha=0.001$ at both temperatures, because diffusion of H_2O molecules to them is hampered owing to strongly imperfect molecular accommodation at the particle surface. Delayed freezing occurs because smaller freezing particles result in smaller initial ice particles. Smaller ice particles, in turn, need longer to deplete the H_2O gas phase and thereby shut off further nucleation. As a result, n_i (and S_i) increases significantly over the SUL or SUL+SUL/MAL cases, as can also be read off Fig. 3.

3.5. Effects of aerosol composition depend on cooling rates

In Fig. 5 we show η as a function of the adiabatic cooling rate for the two particle system SUL+SUL/MAL at selected α for the SUL/MAL particles and T . For $\alpha=0.1$, η is a weak function of dT/dt up to cooling rates of $\sim 20 \text{ K h}^{-1}$. Under these conditions, all particles are close to water equilibrium, and $\eta \approx 0.3$ is caused by differences in the equilibrium aerosol size distributions between SUL and SUL/MAL, see Fig. 2b. At higher cooling rates, non-equilibrium effects create larger differences in η , so that fewer organic-containing particles freeze for $T=215$ and 230 K .

When α is decreased, the range of cooling rates dT/dt within which all particles can be assumed to stay close to equilibrium conditions becomes successively narrower. Clearly, for less hygroscopic organic aerosols, the effect of disparate water uptake is the major factor for their poor homogeneous freezing potential for all conceivable values of dT/dt .

Interestingly, the fraction of organic particles with $\alpha=0.1$ that freeze at 200 K increases at high cooling rates and approaches the limit $\eta=0.5$ (not shown). This is the case under conditions of vigorous cooling, where the freezing conditions are very rapidly surpassed and differences in freezing rates become irrelevant, thereby causing nearly all particles to freeze in the same proportion. This is not observed for smaller α -values.

4. Comparison with atmospheric observations

A large body of mass spectrometric data of the composition of single particles shows that organics are often internally mixed with sulfates (Murphy et al., 1998), similar to our particle type SUL/MAL. The organic fraction varies significantly from almost pristine sulfate particles with only traces of organics to particles with comparable amounts of organic and inorganic species. Therefore, we assume that the theoretical two mode system SUL+SUL/MAL treated above might be regarded as a typical case for upper tropospheric conditions. In this case, SUL might represent particles with only a very small amount of organics, while SUL/MAL represents particles containing a significant organic mass fraction.

Then, our finding that organic-containing aerosols are inefficient at homogeneous ice formation is consistent with more recent mass spectrometric measurements (Cziczo et al., 2004a,b; DeMott et al., 2003). In one study, particles from the clean lower troposphere over the continental United States of America were sampled and processed in the laboratory while in the second study particles were sampled and analyzed in situ in the subtropical upper troposphere.

We note that, on the basis of our model study, these new observations cannot be explained assuming only one internally mixed inorganic/organic particle mode with a fixed solute mole ratio.

Instead, the recent observations can be explained in terms of size differences between two distinct modes of inorganic (\sim SUL) and mixed inorganic/organic

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(~SUL/MAL) aerosol particles. The size effects arise either from initial differences in size distribution or from effects caused by differences in the thermodynamic and hygroscopic particle properties. Referring to Sect. 3.2, uncertainties in our simulations concern the size range over which most of the organic components are distributed and the chemical nature of the tropospheric organic aerosol population.

Here we touch a general problem: atmospheric observations do not yet provide a detailed picture of the size-resolved chemical speciation of organic-containing particles, as well as their mixing state with other particle types. This is why a closer comparison of our results with available observations is not possible at this point.

Ice saturation ratios up to 1.8 have been measured at cold temperatures (Gao et al., 2004) along with the presence of organic-containing particles (Cziczo et al., 2004b). In view of the results shown in Fig. 3, if two distinct modes of the type SUL and SUL/MAL were present during these measurements, then the high S_i values at 200 K could only be explained if the number of SUL particles was exceptionally low ($<0.5 \text{ cm}^{-3}$ according to the estimate given in Sect. 3.3) and the SUL/MAL particles had very low condensation coefficients (of the order 0.001). Additional or alternative explanations include: small-scale temperature oscillations leading to larger peak values of S_i , which are not considered in our calculations but may effect the measured S_i values in the atmosphere (Kärcher and Haag, 2004); differences at low T between various parameterizations for the vapor pressures of ice and supercooled liquid water (Murphy and Koop, submitted, 2004¹); effects of metastable cubic ice on the modeled gas phase relative humidities (Murphy, 2003).

¹Murphy, D. M. and Koop, T.: Review of the vapour pressure of ice and supercooled water for atmospheric applications, Q. J. Roy. Meteor. Soc., submitted, 2004.

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5. Conclusions

The findings of our modeling study are summarized as follows. As before, we refer with “inorganic” to pure inorganic particles and with “organic” to either pure organic or internally mixed organic/inorganic particles.

1. Differences in the sizes of two externally mixed particle modes determine the homogeneous freezing fractions of each mode in a cooling air parcel. If the particles are chemically identical, the larger mode particles freeze first, preventing most of the smaller mode particles from ever nucleating ice. This effect is more pronounced the lower the freezing temperature.

2. If two particle modes have identical sizes, but differ chemically (inorganic versus organic particles), the particles from the organic mode tend to stay less water-rich during cooling and thus stay smaller than inorganic particles, even if the organic particles have high (>0.1) water accommodation coefficients.

In conditions close to local water equilibrium (slow synoptic cooling), where the water activity in each particle is close to the ambient relative humidity, irrespective of its chemical nature, the organic aerosol is inefficient at homogeneous freezing owing to the induced size effects.

At higher cooling rates (e.g., during mesoscale gravity wave activity) particularly at low temperatures, non-equilibrium effects caused by (a) an increased time scale of water condensation, (b) diffusion limitation of water molecules to large particles ($>1\ \mu\text{m}$), and (c) the Kelvin effect for small particles ($<0.1\ \mu\text{m}$) all influence the freezing fraction of organic particles.

3. If organic particles are sufficiently larger than inorganic particles prior to cooling, it might happen that the organic mode particles nucleate ice preferentially over the inorganic mode, despite less efficient water uptake.

4. Besides size, the water accommodation coefficient for organic particles is a crucial factor controlling their ability to freeze homogeneously. Small values (<0.1) slow the rates of increase of water activity and volume of the particles, and thus delay freezing

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relative to inorganic particles, even if organic particles are initially larger and/or cooling rates are slow.

5. In case of vigorous cooling (e.g., in a convective cloud), differences between the freezing rates of organic and inorganic particles caused by size or kinetic effects diminish, if organic condensation coefficients are not substantially smaller than ~ 0.1 . In such situations, nearly all particles freeze in the same proportion.

6. In the absence of inorganic particles, organic aerosol particles with low water condensation coefficients will cause a substantial increase in the freezing saturation ratio at low temperatures (perhaps by up to ~ 0.2), accompanied by an increase in the total number of ice crystals formed. If inorganic particles are present and compete in the freezing process, freezing commences at values characteristic for the inorganic particles unless their number concentrations falls below a (small) critical value.

Recent tropospheric observations indicate that organic particles preferentially remain unfrozen. In view of the above findings, these observations would be consistent with freezing processes initiated in physically separate modes of inorganic and organic particles. Our study thus provides a consistent physical explanation within the framework of the water-activity-based nucleation model if such distinct particle modes were indeed present during the measurements.

A more detailed comparison with observations is precluded by the fact that current atmospheric measurements do not provide all of the details about the organic aerosol number and size, size-resolved chemical composition and hygroscopicity, and mixing state with inorganic species, required to better constrain the model simulations.

We have not considered possible mechanisms that could modify the freezing process in organic aerosol particles. Hydrophilic OH-groups of long chain alcohols could self-assemble into two dimensional crystal-like structures at the surface of aerosol droplets and perhaps lead to increased freezing temperatures, as observed for supercooled liquid water droplets of various size (Gavish et al., 1990; Zobrist et al., 2004). On the other hand, organic surfactants could hamper the uptake of water molecules in aerosol particles by reducing the condensation coefficient (Xiong et al., 1998), thereby reducing

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their ability to freeze homogeneously. Furthermore, partial crystallization in certain organic particles and delayed deliquescence could change the freezing mode from homogeneous to heterogeneous. For comparison, similar effects have been observed in laboratory experiments with pure ammonium sulfate particles (Zuberi et al., 2001; Hung et al., 2002).

Too little basic information is currently available to study all these issues theoretically. Despite these uncertainties, we believe that we have established the most important factors determining the role of organic tropospheric aerosols in homogeneous ice formation in cirrus conditions. While our results may be subject to quantitative changes, we expect the processes outlined here to actually occur in the atmosphere. This may help refine parameterizations of cirrus cloud formation employed in climate models.

Our work provides a convenient framework for future modeling studies related to the formation of cirrus clouds. More laboratory and field observations are required in order to make further headway in quantifying the overall role of organic aerosols in the freezing process and assessing their impact on the tropospheric ice phase.

Acknowledgements. This work was funded, in part, by the European Commission within the Integrated Project “Stratosphere-Climate Links With Emphasis on the UTLS” (SCOUT-O3).

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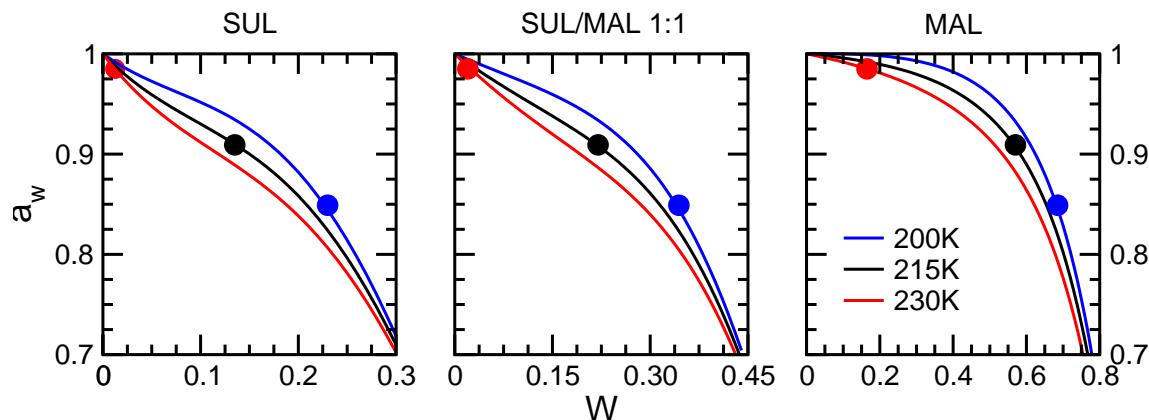


Fig. 1. Water activity as a function of solute mass fraction in aqueous solutions for three selected temperatures. Results are shown for pure sulfuric acid **(a)**, a 1:1 molar mixture of sulfuric acid and malonic acid **(b)**, and pure malonic acid **(c)**. The filled circles indicate the conditions where homogeneous ice nucleation commences according to the water-activity-based freezing model. This model assumes that the freezing particles are in thermodynamic equilibrium with water vapor, i.e., $a_w = RH/100\%$. For any given T , freezing occurs at the same a_w in each particle type, but the corresponding particle volumes ($\propto W$) may differ significantly.

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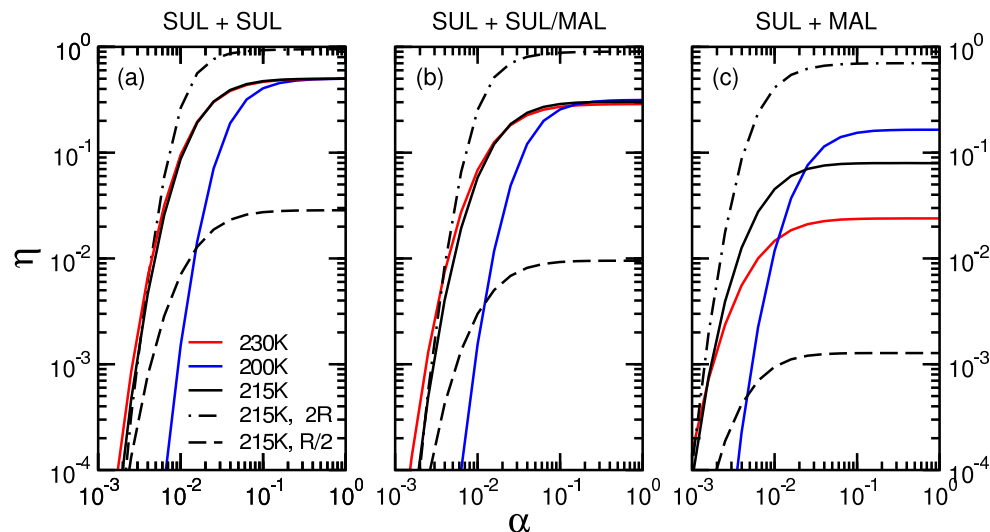


Fig. 2. Number of frozen aerosol particles with variable mass accommodation coefficient relative to the total number of ice particles formed in air parcels cooling at 10 K h^{-1} at different freezing temperatures. In all cases, the aerosol is composed of one pure sulfuric acid particle mode (SUL) with $\alpha=1$, to which another sulfuric acid mode **(a)**, the internally mixed sulfuric acid/malonic acid mode **(b)**, and a mode composed of pure malonic acid **(c)** is added, each with variable α . The solid curves represent cases where the initial dry size distribution of all modes were identical. The dashed (dash-dotted) curves represent cases where the initial dry sizes of the modes with variable α were half (twice) as large.

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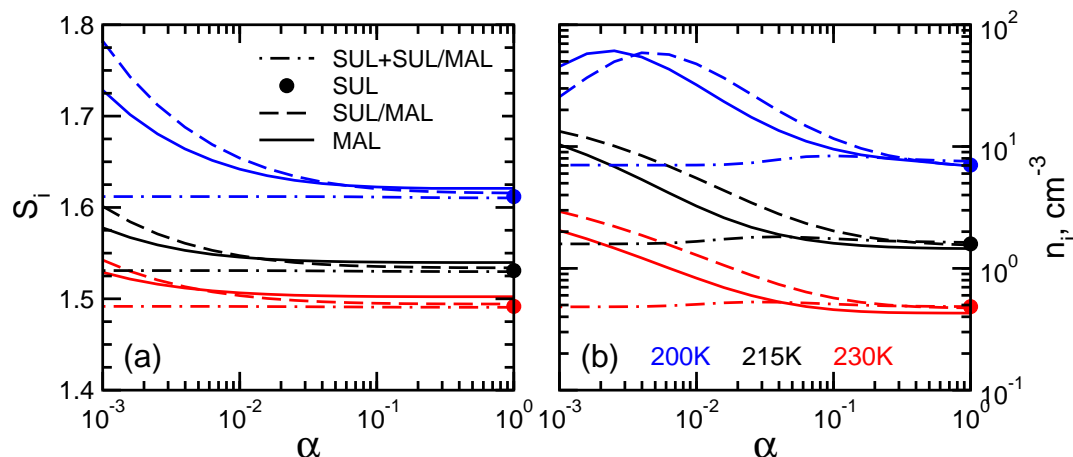


Fig. 3. Peak ice saturation ratio **(a)** and total number of ice crystals nucleated in the cooling air parcels as a function of the mass accommodation coefficient for pure sulfuric acid (filled circles), pure malonic acid (solid curves), internally mixed sulfuric acid/malonic acid particles (dash-dotted curves), and the two particle system containing equal numbers of pure sulfuric acid and internally mixed organic particles.

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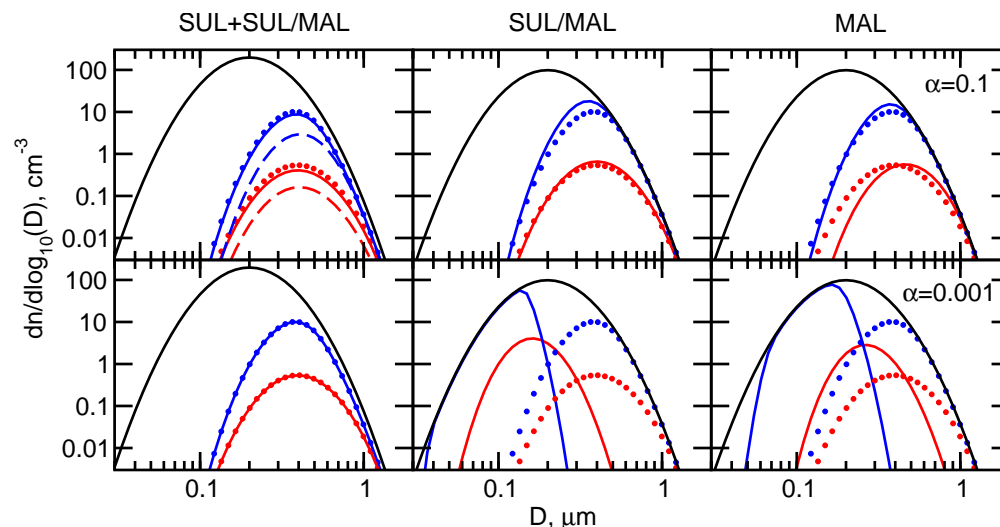


Fig. 4. Initial dry size distributions for the two particle system containing equal numbers of pure sulfuric acid and internally mixed organic particles (SUL+SUL/MAL), internally mixed sulfuric acid/malonic acid particles only (SUL/MAL), and pure malonic acid particles only (MAL), all shown as black curves. Results are given assuming $\alpha=0.1$ ($\alpha=0.001$) for SUL/MAL and MAL in the top (bottom) panel. As before, red (blue) curves denote freezing temperatures of 230 (200) K. The colored solid curves (including the dashed SUL/MAL contribution in the left column that contributes for $\alpha=0.1$ only) are the respective freezing aerosol distributions, defined as the difference of the distributions before and after freezing plotted versus dry particle size. In all figures the freezing distribution for case SUL (with $\alpha=1$) is shown (filled circles) for comparison.

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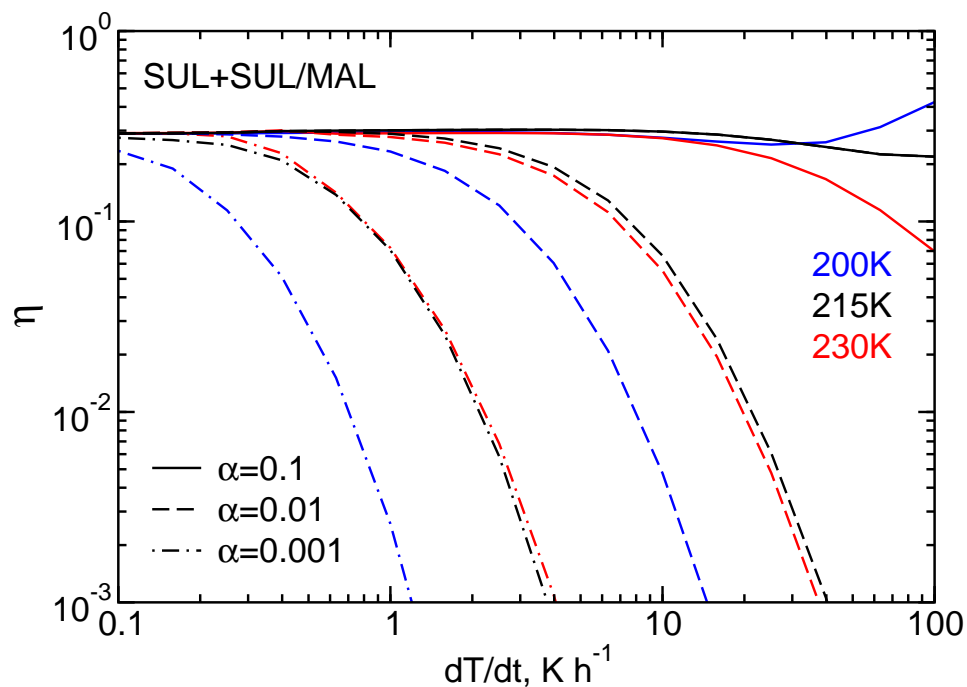


Fig. 5. Fraction of frozen aerosol particles in the two particle system SUL+SUL/MAL versus air parcel cooling rate for selected temperatures and mass accommodation coefficients of the SUL/MAL component.

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